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## **First Principles Calculations on the Diffusion of Cu, Ag and Au Atoms or Aggregates on the Bulk and Surface of Titania**

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<b>14. ABSTRACT</b> This report results from a contract tasking Università Milano Bicocca as follows: The Grantee will investigate with first principle quantum chemical methods the adsorption and diffusion of Cu, Ag and Au species (atoms or small aggregates) on the surface and in the bulk of titania. The Grantee will consider both stoichiometric and reduced titania, with particular attention to the interaction of the metal species with defects and irregularities in the oxide. We will investigate the effect of external electric fields on the diffusion of charged species in the attempt to better understand the behavior of this material in memory/switching devices. The nature of Ag(111)/TiO2 rutile and anatase interfaces, of interest for the design of memristors, has been studied by means of density functional theory (DFT) calculations using various computational approaches. We have considered interfaces where the lattice mismatch of the oxide crystalline phase and the metal electrode does not result in excessive strain. The bonding at the interface is very weak and the charge transfer is negligible for stoichiometric oxides. The formation of O vacancies has a lower cost at the interface with Ag than on the bare titania surface and results in stronger adhesion between the Ag electrode and the reduced TiO2-x oxide. The diffusion of Ag and O atoms/ions across the interface is a thermodynamically unfavorable process which can occur only at high temperatures or under the effect of an external electric field. Once Ag atoms are incorporated in the bulk of TiO2 they can be stabilized in interstitial (more favorable) or substitutional to Ti positions. In both cases Ag is ionized and transfers the valence electron to the host crystal with formation of Ti3+ states. The Ag atoms remain positively charged even when extended Ag chains are formed (nanofilaments). For an Ag filament inside TiO2 to exhibit conductive behavior a higher density of Ag atoms is required but this is hardly possible in the regular bulk crystalline lattice of TiO2 without creating a structural breakdown.					
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## Final report

### First principles calculations on the diffusion of Cu, Ag and Au atoms or aggregates on the bulk and surface of titania

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## Summary

The nature of Ag(111)/TiO<sub>2</sub> rutile and anatase interfaces, of interest for the design of memristors, has been studied by means of density functional theory (DFT) calculations using various computational approaches. We have considered interfaces where the lattice mismatch of the oxide crystalline phase and the metal electrode does not result in excessive strain. The bonding at the interface is very weak and the charge transfer is negligible for stoichiometric oxides. The formation of O vacancies has a lower cost at the interface with Ag than on the bare titania surface and results in stronger adhesion between the Ag electrode and the reduced TiO<sub>2-x</sub> oxide. The diffusion of Ag and O atoms/ions across the interface is a thermodynamically unfavorable process which can occur only at high temperatures or under the effect of an external electric field. Once Ag atoms are incorporated in the bulk of TiO<sub>2</sub> they can be stabilized in interstitial (more favorable) or substitutional to Ti positions. In both cases Ag is ionized and transfers the valence electron to the host crystal with formation of Ti<sup>3+</sup> states. The Ag atoms remain positively charged even when extended Ag chains are formed (nanofilaments). For an Ag filament inside TiO<sub>2</sub> to exhibit conductive behavior a higher density of Ag atoms is required but this is hardly possible in the regular bulk crystalline lattice of TiO<sub>2</sub> without creating a structural breakdown.

## 1.Introduction

Five main technologies are presently under scrutiny for new generation of non volatile memories: (1) phase change memories (PCM) based on chalcogenide glass,<sup>1</sup> (2) memories based on magnetic tunnel junctions and the magnetoresistive effect (MRAM),<sup>2,3</sup> (3) charge trapping memories (CTM) where information is stored in form of charge traps in the nitride layer of a semiconductor-nitride-semiconductor capacitor structure,<sup>4</sup> (4) ferroelectric memories (FeRAM),<sup>5</sup> and (5) transition metal oxide based resistive memories (or memristors, RRAM).<sup>6-17</sup> An aspect common to all these devices is that a material is sandwiched between two electrodes which measure the resistivity of the material hence the memory state of the device. Changes in resistivity can be generated by magnetic fields, heat, or voltage pulses, switching the device from a conductive to a non conductive state.

The origin of the resistive switching in memristors is still matter of debate and nice reviews about this problem can be found in ref. 6 and 18. It is assumed that typical resistive switching is initiated by a voltage-induced partial dielectric breakdown in which Joule heating modifies the material along a discharge filament. The filament may be composed of the metal electrode which is transported into the insulator or due to the formation of sub-oxides. During the reset transition the conductive filament is thermally destroyed by the high local power density. According to another mechanism charge injection and charge displacement effects are at the origin of the phenomenon. The idea is that electronic charges are injected by tunneling at high fields into defect sites present in the insulator. This modifies the electrostatic barrier and the resistance of the oxide. In a variant of this model charge trapping at the interface can affect the height of the Schottky barrier at a metal/semiconductor interface. A third model is that charge injection may result in a insulator-to-metal transition by effect of system doping.

Another mechanism, of more direct interest for this modeling study, is the possibility that ionic transport and red-ox processes are at the basis of the resistive switching. The idea is that the oxidation of the active metal electrode in contact with the oxide phase results in the release of metal ions (e.g.  $\text{Ag}^+$ ). This is followed by the drift of the mobile ions within the oxide layer and subsequent discard at the inert metal counter-electrode. This mechanism should lead to the formation of metal dendrimers inside the oxide which represent the conductive filament when the state of the cell is ON. By reversing the polarity, the filament is then dissolved resetting the system to the OFF state. A variant of this picture is that what diffuses inside the insulating phase are not cations but anions moving in direction of the anode (actually, what is migrating are probably oxygen vacancies towards the catode). This should result in a local change in conductivity.

Clearly, there are many open questions and it is still largely unclear which type of mechanism is responsible for the observed sudden and reversible change in resistivity. There is also

increasing evidence that the nature of the interface between the metal electrodes, typically Ag or Pt, and the thin oxide dielectric (NiO, TiO<sub>2</sub>, perovskites) plays an important role in the process.

Among the various systems proposed there are TiO<sub>2</sub> films of 30-60 nm thickness deposited on Pt or Ag electrodes. Titania has various polymorphs, with rutile being the thermodynamically most stable phase while anatase, more interesting for applications, exists as a metastable phase below about 800 °C. However, titania films can also be amorphous, or can exist as a mixture of amorphous and crystalline phases, with the amorphous component usually increasing by decreasing the film thickness. What is present in both crystalline and amorphous phases is the short range order, as shown by Raman spectra.<sup>19</sup> Amorphous films are preferred in order to eliminate electrical leakage along grain boundaries. Other requirements for ideal materials are a large optical band gap and thermodynamic stability at high temperatures.

Despite the technological importance of the topic, very little work has been done on the side of electronic structure calculations. In a recent paper the rectifying properties of Pt/TiO<sub>2</sub> interfaces have been discussed based on density functional theory (DFT) calculations,<sup>20</sup> but there are not many other examples in the literature. In this work we have considered various models of Ag/TiO<sub>2</sub> interfaces using a first principles DFT supercell approach. Since TiO<sub>2</sub> can be easily reduced resulting in n-type conductivity, we have considered both stoichiometric and reduced interfaces. As it will be shown below, these latter exhibit much larger adhesion energies and are probably more reactive. We also considered the possible interdiffusion of Ag atoms into the oxide phase or of O atoms into the metal electrode in order to verify the thermodynamic cost of injecting atomic species at the metal/oxide boundary. In a second part of the study we have considered the nature of Ag dopants in interstitial and substitutional positions of bulk TiO<sub>2</sub> and the effect of increasing the Ag concentration with formation of Ag nanofilaments inside the crystal.

## 2. Methods, assumptions, procedures

The description of metal/oxide interfaces with DFT is not trivial because of the necessity to treat at the same footing both the metallic (Ag) and the insulating (TiO<sub>2</sub>) phases. Furthermore, the self-interaction problem in DFT leads to an underestimation of the band gap of TiO<sub>2</sub> and to an incorrect description of electron localization of defects like oxygen vacancies.<sup>21</sup> A way to remove the self-interaction problem is to use hybrid exchange-correlation functionals where the Hartree-Fock exchange is mixed in various amounts with the DFT exchange. This works well for bare oxides but hybrid functionals do not describe metals very well<sup>22</sup>, limiting their use in metal/oxide interfaces. Another solution is represented by the DFT+U approach where a set of atomic-like orbitals (here Ti 3d) are treated with a new Hamiltonian which depends on  $U_{\text{eff}} = U - J$ , where  $U$  is a parameter

describing the energy increase for an extra electron on a particular site and  $J$  is the screened exchange energy.

For this work we used a multiple strategy. The calculations dealing with energetic aspects of the Ag/TiO<sub>2</sub> interfaces have been done at the generalized gradient approximation, GGA (PBE exchange–correlation functional<sup>23</sup>). For this part of the study we adopted the VASP program<sup>24,25</sup> which uses a plane wave basis set and a projector augmented wave method (PAW)<sup>26</sup> for the treatment of core electrons. A TiO<sub>2</sub> film of four or five layers thickness was interfaced with three Ag layers; further details are reported in the following sections. With this representation of the Ag(111) surface both the lattice constant, 4.17 Å, and the metal work function, 4.32 eV, are reproduced with acceptable errors (4.09 Å and 4.46 eV are the experimental quantities, respectively). The atoms within the supercell have been relaxed until a 0.01 eV/Å convergence threshold was reached for atomic forces. Brillouin-zone sampling has been performed on a 4x1x1 (rutile) and 2x2x1 (anatase) k-points mesh according to Monkhorst–Pack integration scheme.<sup>27</sup> Electronic structure properties and density of states (DOS) of the Ag/TiO<sub>2</sub> interface have been obtained in selected cases using a DFT+U approach in order to better represent the band gap of TiO<sub>2</sub> and the band offset of the metal and the insulating phases. We used  $U - J = 4$  eV since this was shown for TiO<sub>2</sub><sup>28</sup> to provide results similar to the classical B3LYP hybrid functional<sup>29,30</sup> used for the study of Ag atoms inside the bulk of the oxide (see below). With this  $U$  value the band gap of bulk anatase TiO<sub>2</sub> is 2.81 eV, to be compared with a gap of 2.25 eV obtained at the GGA level and of 3.2 eV in the experiment.

The B3LYP hybrid functional, and a completely different computational setup were used to study Ag atoms incorporated into the bulk of anatase TiO<sub>2</sub>. As it will be discussed below, Ag atoms act as reducing agents with formation of Ag<sup>+</sup> ions and Ti<sup>3+</sup> states which, being localized, give rise to electronic levels in the gap of TiO<sub>2</sub>, an aspect which is not correctly described by pure GGA approaches. We performed spin polarized B3LYP calculations using the CRYSTAL06 code<sup>31</sup> since this approach has been successfully used to describe reduced TiO<sub>2</sub>.<sup>32</sup> The Kohn-Sham orbitals have been expanded in Gaussian Type Orbitals (GTO) and the all-electron basis-sets are 86411(d41)<sup>33</sup> for Ti, 8411(d1)<sup>34</sup> for O, and 311(d31) for Ag.<sup>35</sup> In this latter case an effective core potential was used.<sup>36</sup> We considered two different models of bulk anatase: i) a nearly cubic 2√2x2√2x1 supercell containing 32 Ti and 64 O atoms and ii) a 3x1x2 supercell containing 24 Ti and 48 O atoms. The optimized bulk lattice unit cell parameters were taken from previous B3LYP calculations ( $a = 3.776$  Å, and  $c = 9.866$  Å).<sup>37</sup> The band gap of anatase TiO<sub>2</sub>, 3.9 eV, is overestimated compared to the experimental value, 3.2 eV. Full geometry optimization was performed until the largest component of the ionic forces was less than 5x10<sup>-4</sup> a.u. The reciprocal space is sampled according to a regular

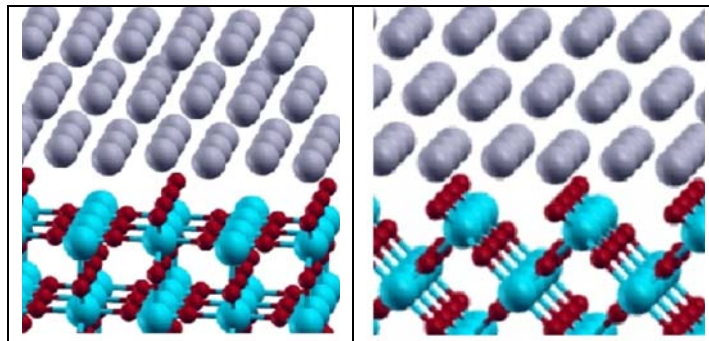
sublattice with a shrinking factor (input IS) of 2 for the larger supercell and of 4 for the smaller one. The DOS curves have been computed with a 4 x 4 x 4 k-point mesh.

### 3. Results and discussion

In real devices the interface between the metal electrode and the insulating film involves a polycrystalline material (Ag) and an amorphous phase ( $\text{TiO}_2$ ). In our modeling study, in order to reduce the complexity of the system, we consider metal and oxide single crystal surfaces. While this allows one to have a microscopic view of the interface structure, it may also result in other problems like the need to create commensurate interfaces where little strain remains after adapting the Ag lattice to that of titania.

#### 3.1 Ag/ $\text{TiO}_2$ interface structures

There are not too many studies dealing with stoichiometric epitaxial films of rutile and anatase  $\text{TiO}_2$  on metal single crystal surfaces. On the contrary, intensive work has been reported by the group of Granozzi on new phases associated to ultrathin titania films on Pt.<sup>38</sup> Recently, a monolayer  $\text{TiO}_2$  film with lepidocrocite structure grown on Ag(100) has been reported.<sup>39</sup> On the theoretical side, Lopez and Norskov<sup>40</sup> studied the Au(111)/ $\text{TiO}_2$ (110) rutile interface which however implies a large modification of the lattice parameter of the gold metal in order to create a commensurate interface. This configuration has been used as a starting point for our study of the Ag(111)/ $\text{TiO}_2$ (110) rutile interface; the Ag(111) slab has been compressed by 7% in the [1-11] direction and expanded by the same amount in the [001] direction. The supercell used is 2x1 and contains 18 Ag atoms and 16  $\text{TiO}_2$  units. The Ag atoms have been placed either on-top of the bridging oxygens of rutile (110), Fig. 1a, or in the regions between them. However, due to the large lattice mismatch, when the structure is relaxed unphysical distortions occur in the metal phase. In particular, a substantial rumpling of the Ag(111) planes occurs due to the strain in the slab. This is shown by the fact that the same distortion is found also for an unsupported Ag(111) film with the same lattice constants. Due to the substantial strain in the structure, this model will be no longer discussed.





a	b
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Fig. 1 – (a) The Ag(111)/TiO<sub>2</sub>(110) rutile interface (O-top configuration). (b) The Ag(111)/TiO<sub>2</sub>(100) rutile interface (O-top configuration).

To reduce the strain we have considered the next most stable rutile surface, the (100) one. Here one can reduce the compression of the Ag film along the [1-11] direction below 5%. The expansion along the [001] direction remains of 7%. The supercell used is 3x1 and contains 18 Ag atoms and 15 TiO<sub>2</sub> units. Also in this case we considered a starting configuration where the Ag atoms are above the bridging oxygens of rutile (100), Fig. 1b.

During geometry relaxation, the metal film undergoes a large structural rearrangement with distortions along the z direction of the Ag planes. However, differently from the previous case, this distortion is due to the chemical interaction of the metal with the oxygen atoms of the TiO<sub>2</sub> surface; the standing along Ag film does not exhibit the same kind of reconstruction. The adhesion energy,  $E_{adh}$ , defined as the energy of the interface structure minus that of the separate components in their optiman geometry, is low, 25.0 meV/Å<sup>2</sup>, the charge transfer from Ag to TiO<sub>2</sub> is negligible,  $9.8 \cdot 10^{-3}$  e/Å<sup>2</sup>, and the interface distance, defined as difference of the average vertical positions of the Ag and of the O or Ti top layers, 2.89 Å, is rather long, Table 1. As shown by the DOS curves obtained at the DFT+U level, Fig. 2a, there is almost no hybridization of the Ag and TiO<sub>2</sub> states, which is consistent with the very small charge transfer at the interface. The Fermi level lies high in the band gap of the oxide. The interface represents a Schottky contact with a conduction band offset from the Fermi energy of 0.8?? eV. However, due to the extremely weak interaction and the absence of O-Ag hybridization, there are almost no metal induced gap states (MIGS).

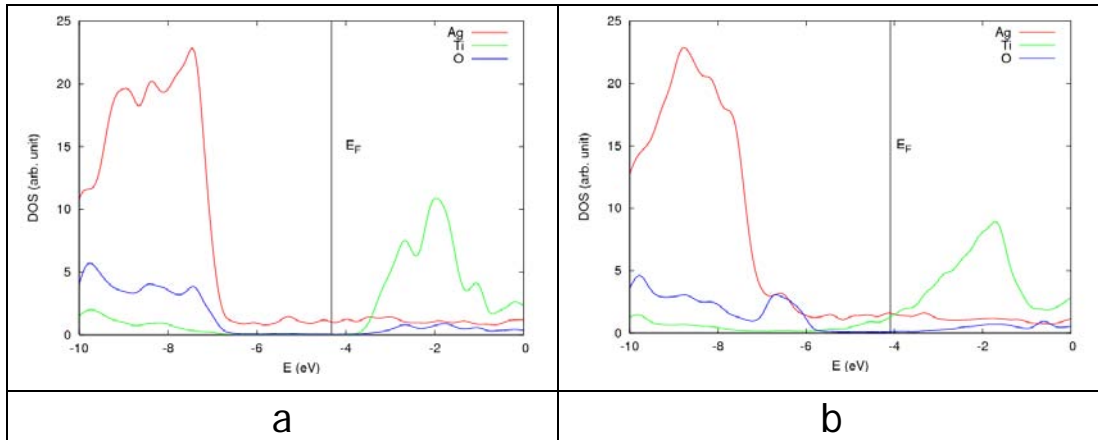


Fig. 2 – DOS curves of (a) the stoichiometric Ag(111)/TiO<sub>2</sub>(100) rutile interface; (b) the reduced

# Ag(111)/TiO<sub>2</sub>(100) rutile interface (DFT+U results)

It is well known that titania is easily reduced. For this reason we have considered also the nature of the interface between a highly reduced rutile (100) surface and Ag(111). All the bridging oxygens of rutile (100) have been removed from the surface and the properties of the Ag(111)/TiO<sub>2-n</sub>(100) rutile interface have been recalculated. The energy required to removed oxygen from the TiO<sub>2</sub> phase and form a reduced Ag/TiO<sub>2-n</sub> interface,  $E_{\text{red}}$ , normalized to the number of removed O atoms per unit cell,  $n$ , is defined as:

$$E_{\text{red}}(\text{Ag}/\text{TiO}_2) = [E(\text{Ag}/\text{TiO}_{2-n}) + n/2 E(\text{O}_2) - E(\text{Ag}/\text{TiO}_2)]/n \quad (1)$$

It should be compared with the same process occurring on the bare TiO<sub>2</sub>(100) surface:

$$E_{\text{red}}(\text{TiO}_2) = [E(\text{TiO}_{2-n}) + n/2 E(\text{O}_2) - E(\text{TiO}_2)]/n \quad (2)$$

While  $E_{\text{red}}(\text{TiO}_2)$  is about 4.3 eV per O atom (small fluctuations are connected to the size of the supercell and the number of TiO<sub>2</sub> layers),  $E_{\text{red}}(\text{Ag}/\text{TiO}_2)$  is 3.84 eV only, indicating that the formation of a metal/oxide interface favors the chemical reduction of the oxide. Furthermore, it has been shown in the literature and confirmed in this study, that the oxygen removal is easier for the titania layer in direct contact with the metal than for internal bulk layers. This result is quite general and has been demonstrated for other metals and oxides.<sup>20,41</sup>

Table 1 – Properties of Ag(111)/TiO<sub>2</sub> interfaces ( $E_{\text{adh}}$  = adhesion energy, CT = charge transfer from Ag to TiO<sub>2</sub>,  $z_{\text{interface}}$  = interface distance<sup>a</sup>)

		supercell	$E_{\text{adh}}$ , meV/Å <sup>2</sup>	CT, e/Å <sup>2</sup>	$z_{\text{interface}}$ , Å
Ag(111)/TiO <sub>2</sub>	Rutile (100)	3x1	25.0	$9.8 \cdot 10^{-3}$	2.89
Ag(111)/TiO <sub>2-x</sub>	Rutile (100)	3x1	62.3	$-29.4 \cdot 10^{-3}$	2.49
AgO <sub>x</sub> (111)/TiO <sub>2-x</sub>	Rutile (100)	3x1	84.0	-	2.48
Ag(111)/TiO <sub>2</sub>	Anatase (001)	$2\sqrt{2} \times 2\sqrt{2}$ r45°	13.1	$9.5 \cdot 10^{-3}$	2.59

a) defined as difference of the average vertical positions of the Ag and of the O or Ti top layers

Not surprisingly, the Ag/TiO<sub>2</sub> interaction becomes much stronger for the reduced surface. The adhesion energy, 62.3 meV/Å<sup>2</sup>, is more than twice that for the stoichiometric interface, the charge transfer is more pronounced and goes in the opposite direction, from TiO<sub>2</sub> to Ag,  $-29.4 \cdot 10^{-3}$  e/Å<sup>2</sup>, and the interface distance is shorter, 2.49 Å, Table 1. This has direct consequences on the DOS curves and in particular results in the presence of MIGS in the band gap of the oxide which are now more pronounced, Fig. 2b. The Fermi level is now above the tails of the bottom of the conduction band, indicating a partial metallization of the rutile (100) surface at this level of

chemical reduction.

So far we have assumed that during the reduction of  $\text{TiO}_2$  the O atoms recombine and leave the sample in form of  $\text{O}_2$  molecules, see eq. (1) and (2). However, at a real interface it is possible that the O atoms are displaced from their lattice positions and diffuse into the bulk of the metallic phase. This process could lead to an intermediate  $\text{Ag}_x\text{O}_y$  phase in contact with a reduced titania layer. A process of this kind could facilitate the generation of  $\text{Ag}^+$  ions to be injected into the oxide phase. To this end, we have considered a simple model where the bridging O atoms of the  $\text{TiO}_2(100)$  rutile surface have been removed and incorporated into the Ag metal in interstitial positions between the first and the second layers of  $\text{Ag}(111)$ . We have considered two supercells of different dimensions, a  $3 \times 1$  cell, Fig. 3a, and a  $3 \times 2$  supercell, Fig. 3b. In the first case all the bridging O atoms were moved into the Ag metal, while in the second case only one every two O atoms has been displaced, Fig. 3b.

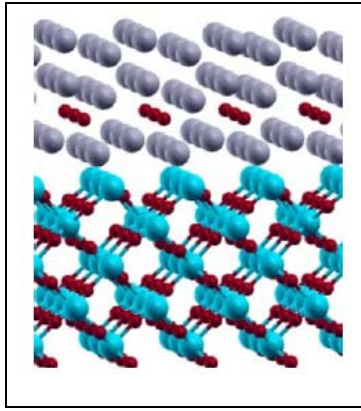


Fig. 3 – Formation of a reduced  $\text{Ag}(111)/\text{TiO}_2(100)$  rutile interface and of an oxygen layer inside the Ag electrode

This process leads to a partly reduced titania phase,  $\text{TiO}_{2-n}$ , and a weakly oxidized metal phase,  $\text{AgO}_n$ . The corresponding formation energy,  $E_{\text{red-ox}}$ , normalized to the number of displaced O atoms, is defined as:

$$E_{\text{red-ox}}(\text{Ag}/\text{TiO}_2) = [E(\text{AgO}_n/\text{TiO}_{2-n}) - E(\text{Ag}/\text{TiO}_2)]/n \quad (3)$$

After relaxation, the O atoms, initially placed in octahedral cavities, have moved into (distorted) tetrahedral cavities. This is also the site occupied by O atoms in the native  $\text{Ag}_2\text{O}$  oxide.  $E_{\text{red-ox}}$  is still positive and rather large. For the small supercell, corresponding to high O concentration,  $E_{\text{red-ox}}$  is 3.73 eV; for comparison,  $E_{\text{red}}$  value for the  $\text{Ag}/\text{TiO}_2$  interface, eq. (1), is 3.84 eV, i.e. only slightly

larger indicating little gain when O atoms are injected into the Ag electrode compared to the formation of gas-phase O<sub>2</sub>. For the larger supercell (smaller concentration of O interstitials),  $E_{\text{red-ox}}$  decreases to 3.03 eV, still indicating an endothermic process. The reason can be understood by considering the low affinity of Ag for O. If we place an O atom in the bulk of Ag and we take  $\frac{1}{2}\text{O}_2$  as a reference, we find that the process is endothermic by 0.47 eV and 0.65 eV for an O atom occupying an octahedral and a tetrahedral cavity, respectively. Clearly, it is not possible to compensate the high energy cost to remove oxygen from the titania surface by incorporating it into silver. The consequence, however, is that the adhesion energy, computed as the energy required to separate the AgO<sub>n</sub> and the TiO<sub>2-n</sub> layers, increases to 86.4 meV/Å<sup>2</sup>, and that an AgO<sub>n</sub> phase is formed. Here the Ag atoms are partly oxidized, an effect which could favor the generation of Ag<sup>+</sup> ions and their diffusion into the oxide.

In order to study these processes we have considered another titania surface, the (001) face of anatase, which has the characteristic to be nearly commensurate with the Ag(111) surface. The (001) is the second most stable anatase surface, and it has been chosen because one can identify a square unit cell where the lattice mismatch at the interface with Ag(111) is of 1.8% only. This  $2\sqrt{2} \times 2\sqrt{2}$  r45° unit cell contains 141 atoms (45 Ag and 32 TiO<sub>2</sub> units), Fig. 4a-c, and is about twice that used for the Ag(111)/rutile interfaces.

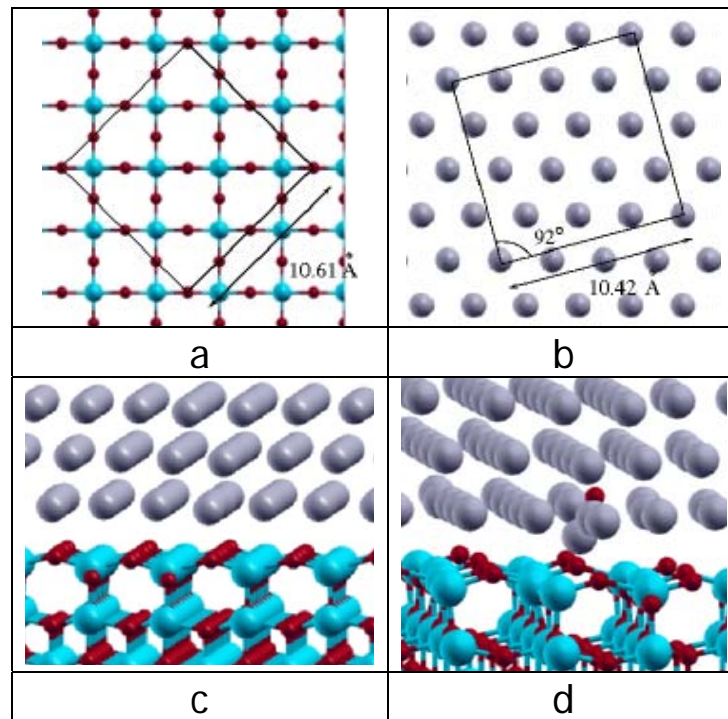


Fig. 4 – The Ag(111)/TiO<sub>2</sub>(001) anatase interface. (a) Surface unit cell of anatase (001); (b) surface

unit cell of Ag(111); (c) side view; (d) Diffusion of an O atom from the oxide to the metal phase.

After optimizing the geometry there is no sign of rumpling or distortions inside the Ag layer. This is also because the interaction of the two components is quite weak, with an adhesion energy of  $13.1 \text{ meV}/\text{\AA}^2$  only, a charge transfer from Ag to  $\text{TiO}_2$  of  $9.5 \cdot 10^{-3} \text{ e}/\text{\AA}^2$ , and an interface distance of  $2.59 \text{ \AA}$ , Table 1. The DOS curves obtained at the DFT+U level are given in Fig. 5.

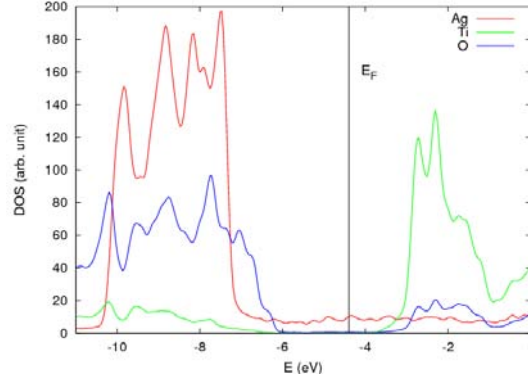


Fig. 5 - DOS Ag(111)/TiO<sub>2</sub> anatase (DFT+U result)

As for the stoichiometric Ag(111)/TiO<sub>2</sub>(100) rutile interface, there is almost no hybridization of the Ag and TiO<sub>2</sub> states, which is consistent with the negligible charge transfer. The Fermi level lies about 2 eV above the top of the O 2p valence band. However, due to the extremely weak interaction, there are no metal induced gap states. In short, this interface structure has virtually no strain but has also no chemical interactions at the interface, making injections of atoms or ions into one of the two phases more difficult.

This aspect has been investigated by studying the same processes described above for the Ag-rutile surface. In this case, however, thanks to the large dimensions of the supercell, we can model the displacement of isolated O atoms of the TiO<sub>2</sub> surface and their incorporation into the Ag electrode. The first step has been the calculation of the formation energy of an oxygen vacancy on the bulk terminated TiO<sub>2</sub>(001) anatase surface. This is 2.93 eV when the O atom is removed from the first layer and 3.98 eV when O is taken from a bulk layer (notice that the (001) anatase surface in vacuum undergoes a strong relaxation so that the formation energy of a vacancy for the relaxed surface is 4.3-4.6 eV,<sup>42</sup> depending on the layer that is reduced). The low value of the vacancy formation energy for the top layer of the unreconstructed TiO<sub>2</sub>(001) surface reported above, 2.93 eV, is thus somewhat artificial and a better estimate is that computed when oxygen is removed from subsurface layers, nearly 4 eV.

We considered the Ag(111)/TiO<sub>2</sub>(001) interface and studied the cost of reducing titania and

simultaneously oxidizing silver. This was done by displacing a single O atom from TiO<sub>2</sub> and including it in an interstitial subsurface site of Ag(111), Fig. 4d. The total energy of this rex-ox system is 2.72 eV higher than the non-defective interface. Depending on which O atom is removed, this energy changes slightly but never more than 0.1 eV. Thus, also in this case we find that the process is endothermic and can occur only at high temperatures or under the effect of an high voltage so that substantial energy barriers can be overcome. On the other hand, the energy required to move O into the metal is lower than that needed to form ½ O<sub>2</sub> in gas-phase. Therefore, any reduction process occurring once the interface is formed will result in partial oxidation of the Ag layer rather than in release of gas-phase oxygen.

When an O vacancy is created on anatase TiO<sub>2</sub>(001), an Ag atom is strongly displaced from the interface towards the vacancy, Fig. 4d. This Ag atom is slightly positively charged, according to the Bader analysis, suggesting that the presence of O vacancies at the interface could represent a channel for the diffusion of positive Ag ions into the oxide.

In a similar way, we considered the energy required to move an Ag atom from the metal into the oxide, i.e. the inverse process with respect to the O diffusion. To this end, an Ag atom taken from the perfect interface has been included in a interstitial cavity of anatase. We found that the Ag species is ionized, as shown by a Bader charge of +0.52 (see also § 3.2). However, during the geometry optimization the Ag atom moves back to its original position restoring the non-defective interface. This is a clear sign that the process is rather endothermic, and that diffusion of Ag is possible only under the effect of external driving forces like those provided by an applied voltage.

### 3.2 Nature of Ag atoms incorporated into bulk anatase

The presence of Ag atoms inside the bulk of anatase TiO<sub>2</sub> and their effect on the electronic structure of the system has been investigated by performing supercell calculations with the CRYSTA06 code and the B3LYP exchange-correlation functional. We considered two possible sites where the Ag atoms are placed, substitutional to Ti or in interstitial cavities. When Ag is substitutional to Ti it is coordinated to six neighboring oxygens via two long apical and four short equatorial bonds of 2.22 and 2.03 Å respectively. The local structure remains that of undoped anatase except for the bond lengths that are about 0.2 and 0.1 Å longer. While Ti in TiO<sub>2</sub> is formally +IV, the Ag atom can only partly supply the electrons needed to fill the valence of the O atoms. When Ag substitutes a Ti atom, Fig. 6a, is formally in a +II oxidation state (3d<sup>9</sup> configuration), with an hole in the 3d<sub>z<sup>2</sup></sub> orbital. The fact that Ag is only a two-electron donor, results in two holes in the 2p levels of the O atoms, one fully localized and one more delocalized, Fig. 6b. Both doublet and quartet spin configurations have been considered, with this latter only slightly lower in energy (by 0.03 eV). However, the energy

cost to remove a Ti atom from the lattice and bring it to the gas-phase and replace it with Ag is extremely high, 22.6 eV. Of course, a much lower energy is expected if the Ti atom, instead of being removed from the crystal, is displaced into an interstitial cavity.

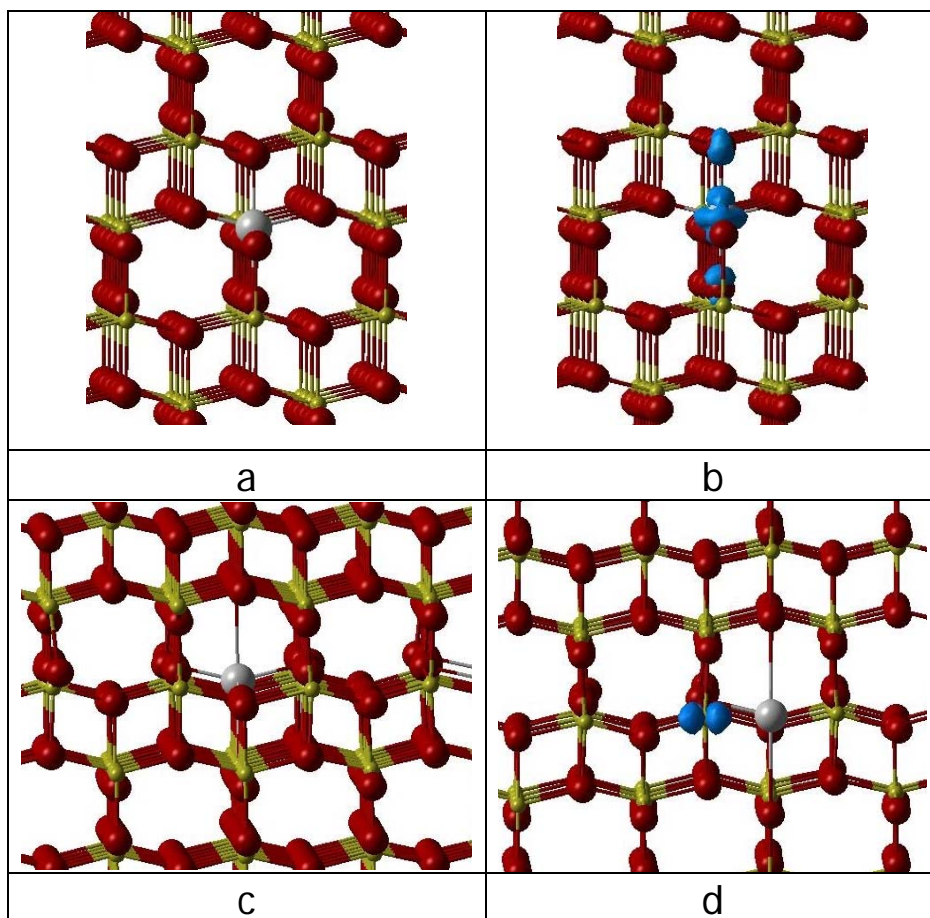


Fig. 6 – (a) Structure and (b) spin distribution of a Ag atom substitutional to Ti in bulk anatase; (c) structure and (d) spin distribution of an interstitial Ag atom in bulk anatase

There are various possible positions where the Ti atom can be accommodated and their total energies have been tested. In the most stable site, Ti is coordinated to five O atoms. The overall energy cost to replace a lattice Ti atom with an Ag atom and to displace it into an interstitial site is 2.4 eV, an energy which can be easily provided during thermal treatment of the sample or under an applied voltage.

Quite interesting from the point of view of the stability is the Ag interstitial species, Fig. 6c. The formation energy, defined as the energy required to include a gas-phase Ag atom into the bulk of anatase, is 1.1 eV, indicating a moderately endothermic process. However, the structure where Ag is interstitial and Ti occupies a lattice position is 1.3 eV lower in energy than that described above where the two atoms have interchanged their positions. This shows unambiguously the preference



of Ag for interstitial sites. In the optimized structure Ag assumes a distorted square planar coordination with O atoms at about 2.2 Å while the apical O atom is 2.93 Å apart, Fig. 6c. From the electronic point of view, there is clear evidence that the Ag atom acts as a reducing agent forming a  $\text{Ag}^+$  ion, Fig. 7. The Ag 5s electron is transferred to the bottom of the conduction band which, being formed of Ti 3d states, leads to the formation of a localized  $\text{Ti}^{3+} (3d_{xy})^1$  species, Fig. 6d and Fig. 7. In particular, the electron is localized on a Ti ion nearest neighbor of the interstitial Ag.

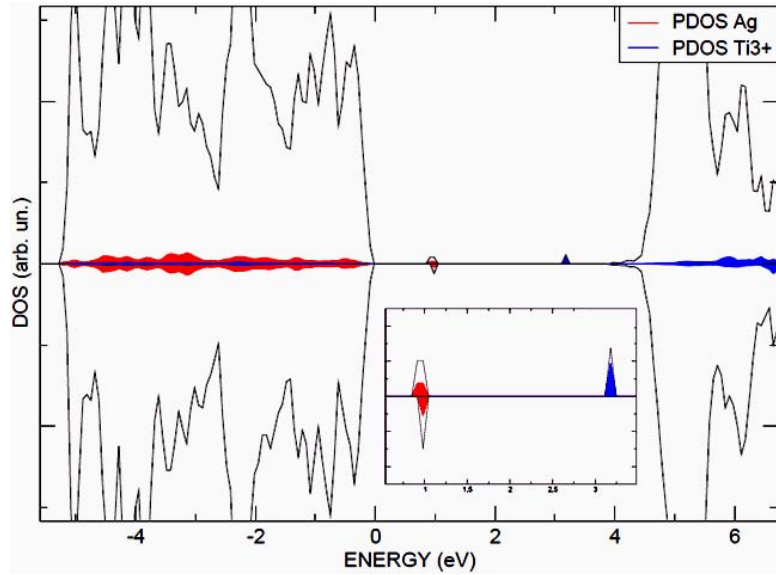


Fig. 7 – Density of states of Ag interstitial

These results provide clear evidence that an isolated Ag atom inside anatase  $\text{TiO}_2$  prefers interstitial positions, loses the 5s valence electron, and is in a positive oxidation state. Only if the density of the incorporated atoms increases, they may switch to a neutral state which could lead to the formation of a metallic “filament”. This mechanism will compete with the tendency of Ti 3d orbitals to trap electrons and form  $\text{Ti}^{3+}$  states.

In order to verify this possibility we have designed a different  $3 \times 1 \times 2$  supercell (see Computational method) which allows one to have Ag atoms at shorter distances (the Ag-Ag distances are 3.78 Å). This could result in the formation of a band due to the overlap of the Ag 5s levels and, possibly, in the formation of a metallic wire. We performed this test for both substitutional and interstitial Ag, Fig. 8. For the filament model created by the repetition of substitutional Ag atoms we found a similar electronic and geometric structure as for an isolated species. Ag has a distorted octahedral coordination and the formation energy is still very high. The absence of a direct orbital interaction among the Ag atoms indicates that it is not possible to form an



Ag nanowire by substitutional defects mainly because the Ag-Ag separation is still too large.

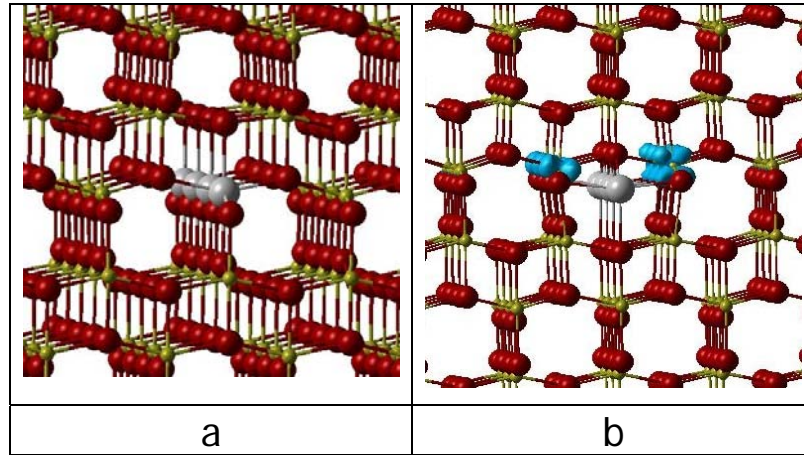


Fig. 8 – (a) Chain of substitutional Ag atoms in anatase  $\text{TiO}_2$  and (b) chain of interstitial Ag atoms in anatase  $\text{TiO}_2$  (the plot shows the spin density).

Also the chain of interstitial Ag atoms does not exhibit a metallic character. The nature of the individual components is that of an  $\text{Ag}^+$  ion. The only differences with respect to the isolated Ag case are that (i) from a structural point of view there is a displacement at the center of square planar pyramid of the Ag atom that becomes five-coordinated and (ii) from the side of the electronic structure the unpaired electron is localized on two Ti atoms and occupies a  $3d_{xy}$  atomic orbital of one Ti neighbor and a  $3d_{yz}$  orbital of the other Ti neighbor, Fig. 8b. With respect to an isolated Ag atom the formation of the chain leads to a small energy gain of 0.39 eV/Ag atom, suggesting that a small but non negligible attractive interaction occurs among the Ag interstitials and that the inclusion of more silver could result in the formation of a metallic wire.

The amount of Ag incorporated in the oxide has been increased by including two Ag atoms in the same supercell, one substitutional to Ti,  $\text{Ag}_{\text{sub}}$ , and one in interstitial positions,  $\text{Ag}_{\text{int}}$ , Fig. 9. In this way the Ag-Ag distance becomes 2.75 Å, not far from that of bulk silver, 2.88 Å. The resulting Ag wire has a zig-zag structure, Fig. 9. It is interesting to note that the same structure, i.e. a zig-zag chain, is adopted by a free Ag wire, not embedded in the oxide. This structure is more favorable than a linear Ag chain; furthermore, the geometry optimization leads to small changes in the Ag-Ag distances (2.61 and 2.65 Å) which are typical of a Peierls distortion in one-dimensional conductors. The free Ag zig-zag wire exhibits 5s density of states at the Fermi level, typical of a metal. Things are quite different when we consider the Ag wire inside  $\text{TiO}_2$ . In fact, in the DOS (not reported) we observe the appearance of an occupied state (spin polarized,  $\alpha$  component) with O character just above the top of the  $\text{TiO}_2$  valence band and close to the Fermi level. This is because the Ag atoms are in positive oxidation state, each acting as one-electron donor. However, the two Ag atoms in the

supercell are not sufficient to compensate for the missing Ti atom (one of the two Ag atoms replaces a lattice Ti atom). As a consequence, two holes are present in the O 2p states, partly mixed with the Ag 4d states. Thus, despite the formation of a continuous Ag wire there is no sign of the appearance of associated conductive states. The Ag 5s band remains empty and well above the bottom of the TiO<sub>2</sub> conduction band.

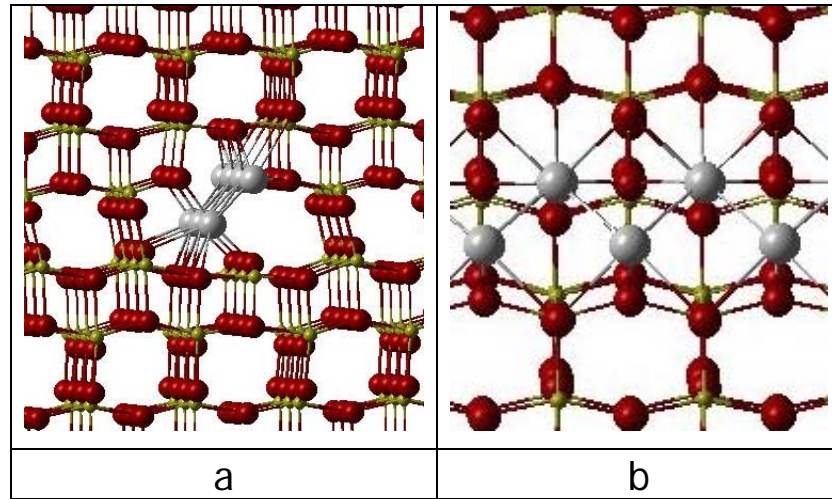


Fig. 9 – Zig-zag chain of Ag interstitial and Ag substitutional in bulk anatase. (a) front view; (b) side view.

To remove the problem of electron deficiency originating from the replacement of one Ti with two Ag atoms per unit cell, we have considered a structure where also an O vacancy has been created. The rationale is that the electron deficiency (holes in the valence band of TiO<sub>2</sub>) can be compensated by creating an O vacancy, a two-electron center associated to the formation of two Ti<sup>3+</sup> ions. Indeed, when we create the O vacancy there are no more holes in the TiO<sub>2</sub> valence band and the system is electrically compensated. This is relevant because we have now a system where a continuous chain of Ag atoms has been created without perturbing in a major way the electronic structure of the anatase host crystal. If one now injects one electron in the system, there are two possibilities: (1) the extra electron enters in the band generated by the Ag 5s levels, thus giving metallic character to the Ag wire; (2) the electron prefers to occupy the Ti empty 3d states which contribute to the bottom of the conduction band of TiO<sub>2</sub>. This possibility has been checked by performing a calculation for the Ag-doped anatase supercell where one extra electron has been added (this results in a charged supercell which requires the use of a background of charge in the calculation). The analysis of the DOS clearly shows that the extra electron prefers to occupy Ti 3d states (formation of Ti<sup>3+</sup>) instead of the Ag 5s band which remains higher in energy.

In conclusion, there is a strong tendency for silver to be stabilized as positive ion inside the bulk of anatase, and this remains true even for densely packed one-dimensional chains. This means that the screening of the positive charge from the surrounding oxide is rather efficient so as to allow the presence of an array of ions in this configuration. Probably a higher concentration of Ag inside the material is needed in order to reach metallization.

#### 4. Conclusions

In this work we have considered simplified models of Ag(111)/TiO<sub>2</sub> interfaces. These systems are of relevance for the design of memristor devices. The focus has been on the following aspects.

(1) We first considered models of the Ag/TiO<sub>2</sub> interface where the lattice mismatch between the two phases is below a few % in order to reduce the strain. This is important in our calculations since we are dealing with single crystal phases and the presence of a large strain in the material can result in unphysical structural distortions. We have found that the anatase (001) face has a good lattice mismatch with the Ag(111) surface provided that a  $2\sqrt{2} \times 2\sqrt{2}$   $\times 45^\circ$  cell is considered. We also analysed the interface of the rutile (100) face with Ag(111) where, however, a substantial strain is still present. In both cases the bonding at the interface is very weak for a stoichiometric oxide, and the charge transfer is negligible. Stronger interfaces are formed when reduced phases of the oxide are considered. In particular, in agreement with previous work, we find that the formation energy of a single O vacancy or of an array of O vacancies has a lower cost at the interface with Ag than on the bare titania surface.

(2) Once the nature of the metal/oxide interface has been determined, we have considered the process of incorporation of O atoms in the metal electrode or of Ag atom in the oxide layer. Both processes imply relatively high formation energies. This is due on one side to the relatively modest affinity of Ag for O ( $\Delta H^\circ(\text{Ag}_2\text{O}) = -31.1$  KJ/mol) compared to that of Ti ( $\Delta H^\circ(\text{TiO}_2) = -944.0$  KJ/mol) and on the other side to the small size of the interstitial cavities present in the bulk of anatase and rutile TiO<sub>2</sub>. The Ag atom inside these cavities is compressed and its steric repulsion with the surrounding is significant. The diffusion of Ag and O atoms/ions across the interface is therefore a thermodynamically unfavorable process which can occur only at high temperatures or under the effect of an external electric field and that could be greatly facilitated by the presence of point defects (vacancies), extended defects (grain boundaries), or by the formation of an amorphous phase of the oxide where larger cavities may exist.

(3) Assuming that Ag atoms have penetrated into the bulk oxide, we have considered their electronic nature. We have studied both isolated Ag atoms in interstitial or substitutional to Ti positions, or higher concentrations of Ag atoms resulting in the formation of dense arrays

(nanofilaments). In all cases we observe a tendency of Ag to be ionized and transfer the valence electron to the host crystal. This is in part a consequence of the steric repulsion described above since the transfer of the Ag 5s electron to the empty Ti 3d states strongly contributes to reduce the repulsion. We also observe a very efficient screening of the positively charged Ag ions so that they remain in this electronic situation even when the Ag-Ag distances are short and extended chains are formed. Even when extra electrons are added to the system they do not enter in the Ag-Ag conducting state but rather prefer to occupy localized Ti 3d states at the bottom of the TiO<sub>2</sub> conduction band. This suggests that for an Ag filament inside TiO<sub>2</sub> to exhibit conductive behavior a higher density of Ag atoms is required in order to form a thicker metallic wire. This is hardly possible in the regular bulk lattice of TiO<sub>2</sub> without creating a structural breakdown.

Aspects which have not been considered in this work and that could significantly affect the phenomena described are the role of O vacancies and their accumulation at the interface, the change of the properties when an amorphous oxide is considered and the role of an external electric field in promoting diffusion of ionic species across the interface. All these effects are expected to lower substantially the energy barriers involved in ion diffusion and in the generation of metal dendrimers inside the oxide structure.

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